

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



(12) UK Patent Application (19) GB (11) 2 351 979 (13) A

(43) Date of A Publication 17.01.2001

(21) Application No 9916322.2

(22) Date of Filing 12.07.1999

(71) Applicant(s)  
Unilever Plc  
(Incorporated in the United Kingdom)  
Unilever House, Blackfriars, LONDON, EC4P 4BQ,  
United Kingdom

(72) Inventor(s)  
Masaaki Arai  
Yukiko Iwamoto  
Mitsunobu Kobayashi

(74) Agent and/or Address for Service  
Peter William Elliott  
Unilever Plc, Patent Division, Colworth House,  
Sharnbrook, BEDFORD, MK44 1LQ, United Kingdom

(51) INT CL<sup>7</sup>  
C11D 3/20 // A61K 7/50

(52) UK CL (Edition S )  
C5D DHG D104 D120 D121 D123 D125 D132 D141 D142  
D162 D166 D179 D182

(56) Documents Cited  
US 5496489 A  
Derwent Abstract No 1996-184676 [19] relating to  
JP080059455 (Kao) 05.03.1996

(58) Field of Search  
UK CL (Edition R ) C5D DHF DHG DHX DHZ DJB DJC  
DJX D132  
INT CL<sup>7</sup> C11D 3/20  
Online: WPI EPODOC PAJ

(54) Abstract Title  
Liquid composition having improved low temperature stability comprising soap, anionic and amphoteric surfactants

(57) The composition has a mixture of isoprene glycol and dipropylene glycol which have been found unexpectedly to significantly retard freezing. The composition also includes soap, sodium lauryl ether sulfate, cocamido propyl betaine, glycerin, EDTA, perfume and water, and is used particularly as a shower gel.

GB 2 351 979 A

16834 U.S. PAT. 10/772824



020504

LIQUID COMPOSITION HAVING IMPROVED LOW TEMPERATURE  
STABILITY COMPRISING SOAP, ANIONIC AND AMPHOTERIC  
SURFACTANTS

5    Field of the Invention

          The present invention relates to liquid compositions used in skin cleansing  
or shower gel compositions. In particular, it relates to compositions comprising  
fatty acid soap (which may be added directly or prepared in situ from free fatty  
10    acid and salts), anionic and amphoteric/zwitterionic surfactant systems.

Background of the Invention

          Personal wash shower gel compositions comprising fatty acid soap,  
15    anionic and amphoteric/zwitterionic surfactants are not new. In low temperatures  
(e.g., 0°C and below), however, the compositions tend to freeze and therefor  
cannot be readily pumped or removed out of their containers.

          Use of isoprene glycol or dipropylene glycol alone (e.g., level of even 9%  
20    by weight of either alone) does not remedy the freezing problem.

          Unexpectedly, applicants have found that if both isoprene glycol and  
dipropylene glycol are used together in a soap, anionic amphoteric/zwitterionic  
system at certain critical ratios, the compositions do not freeze and can be  
25    pumped out of containers in which they are found.

Brief Summary of the Invention

          The present invention relates to an aqueous liquid shower gel composition  
30    comprising:

- (1)    1% to 20% by wt., preferably 2% to 18%, and most preferably 5% to  
          18% by wt. of a C<sub>12</sub> to C<sub>24</sub> fatty acid or mixture of fatty acid;

- (2) 1-10% by wt. of an alkali metal source (e.g., alkali metal hydroxide, alkali metal carbonate); mono-, di- or triethanolamine salts; salts of C<sub>2</sub>-C<sub>4</sub> alkylamines etc.) which reacts with free fatty acids to form soap in situ;
- 5 (3) 1% to 20%, preferably 5 to 15% by wt. of one or more anionic surfactants;
- (4) 1% to 15%, preferably 1% to 10% by weight of an amphoteric/zwitterionic surfactant;
- (5) about 1% to 7% by wt. isoprene glycol; and
- 10 (6) about 2% to 8% dialkylene glycol, preferably 4% to 8% dipropylene glycol;

wherein said composition does not freeze at temperatures as low as -5°C, even as low as -10°C; and wherein compositions having viscosity of 50 cps (measured at 10s<sup>-1</sup>), preferably 100 to 3000 cps, more preferably 100 to 1000 cps, most preferably 300 to 800 cps can be pumped at these temperatures.

15

Alternatively, the "soaps" may be introduced directly into the compositions rather than being prepared in situ. In this case, components (1) and (2) would comprise 1 to 20% by wt. "soap" and (3)-(6) will be the same.

20

#### Detailed Description of the Invention

The present invention relates to an aqueous liquid shower gel compositions comprising fatty acid soap (e.g., formed from alkali metal source and fatty acid), anionic and amphoteric/zwitterionic surfactant.

25

A problem with such liquids is that, under cold weather or cold storage conditions, the composition freeze such that they can not be pumped or dispensed from the container holding the liquids.

30

Unexpectedly, applicants have found that combination of isoprene glycol and dialkylene glycol (preferably dipropylene glycol), when used in certain

amounts, allows composition to be dispensed/pumped even under conditions in which the compositions normally would freeze.

5 More particularly, using compositions of invention, the compositions will not freeze at temperatures as low as  $-5^{\circ}\text{C}$  and even as low as  $-10^{\circ}\text{C}$ . Compositions have viscosity of 50 to 8000 cps (measured at  $10\text{S}^{-1}$ ), preferably 100 to 3000 cps, more preferably 100 to 1000 cps and most preferably 300 to 800 cps.

10 Viscosity measurements were taken at  $25^{\circ}\text{C}$  at 12 rpm for 30 seconds using Spindle 62, digital viscometer: LVTDV-II (Brookfield).

Compositions of the invention are set out in more detail below.

15 Free Fatty Acid and Neutralizer

The composition of the invention may comprise a  $\text{C}_{12}\text{-C}_{22}$ , preferably  $\text{C}_{12}\text{-C}_{18}$  free fatty acid or mixtures of such fatty acids. Examples of fatty acids which may be used include lauric ( $\text{C}_{12}$ ), myristic ( $\text{C}_{14}$ ), palmitic ( $\text{C}_{16}$ ), stearic ( $\text{C}_{18}$ )  
20 or mixtures thereof.

Generally, when such fatty acids are neutralized using, for example, alkali metal hydroxide or carbonate, fatty acid soaps are made. Examples of compounds which may be used to neutralize are alkali metal hydroxide or  
25 carbonates.

If introduced as separate elements, free fatty acid comprises 1-20%, preferably 2-18% by wt. of the composition, and neutralizing agent comprises 1-10% by wt. of the composition.

30

## Soap

Alternatively, the "soap" may be introduced directly into the composition.

5       The term "soap" is used herein in its popular sense, i.e. the alkali metal or alkanol ammonium salts of aliphatic alkane- or alkene monocarboxylic acids. Sodium potassium mono-, di- and tri-ethanol ammonium cations, or combinations thereof, are suitable for purposes of this invention. In general, sodium soaps are used in the compositions of this invention, but from about 1% to about 25% of the  
10 soap may be potassium soaps. The soaps useful herein are the well known alkali metal salts of natural or synthetic aliphatic (alkanoic or alkenoic) acids having about 12 to 22 carbon atoms, preferably about 12 to about 18 carbon atoms. They may be described as alkali metal carboxylates of acrylic hydrocarbons having about 12 to about 22 carbon atoms.

15       Soaps having the fatty acid distribution of coconut oil may provide the lower end of the broad molecular weight range. Those soaps having the fatty acid distribution of peanut or rapeseed oil, or their hydrogenated derivatives may provide the upper end of the broad molecular weight range.

20       It is preferred to use soaps having the fatty acid distribution of coconut oil or tallow, or mixtures thereof, since these are among the more readily available fats. The proportion of fatty acids having at least 12 carbon atoms in coconut oil soap is about 85%. This proportion will be greater when mixtures of coconut oil  
25 and fats such as tallow, palm oil or non-tropical nut oils or fats are used, wherein the principle chain lengths are  $C_{16}$  and higher. Preferred soap for use in the compositions of this invention has at least about 85% fatty acids having about 12 to 18 carbon atoms.

30       Coconut oil employed for the soap may be substituted in whole or in part by other "high-alluric" oils, that is, oils or fats wherein at least 50% of the total fatty acids are composed of lauric or myristic acids and mixtures thereof. These

oils are generally exemplified by the tropical nut oils of the coconut oil class. For instance, they include: palm kernel oil, babasu oil, ouricuri oil, tucum oil, cohune nut oil, muru-muru oil, jaboty kernel oil, khahan kernel oil, dika nut oil, and ucuhuba butter.

5

A preferred soap is a mixture of about 15% to about 20% coconut oil and about 80% to about 85% tallow. These mixtures contain about 95% fatty acids having about 12 to about 18 carbon atoms. The soap may be prepared from coconut oil, in which case the fatty acid content is about 85% of C<sub>12</sub>-C<sub>18</sub> chain lengths.

10

The soaps may contain unsaturation in accordance with commercially acceptable standards. Excessive unsaturation is normally avoided.

15

Soaps may be made by the classic kettle boiling process or modern continuous soap manufacturing processes wherein natural fats and oils such as tallow or coconut oil or their equivalents are saponified with an alkali metal hydroxide using procedures well known to those skilled in the art. Alternatively, the soaps may be made by neutralizing fatty acids, such as lauric (C<sub>12</sub>), myristic (C<sub>14</sub>), palmitic (C<sub>16</sub>), or stearic (C<sub>18</sub>) acids with an alkali metal hydroxide or carbonate.

20

### Anionic

25

The anionic detergent active which may be used may be aliphatic sulfonates, such as a primary alkane (e.g. C<sub>8</sub>-C<sub>22</sub>) sulfonate, primary alkane (e.g., C<sub>8</sub>-C<sub>22</sub>), disulfonate, C<sub>8</sub>-C<sub>22</sub> alkene sulfonate, C<sub>8</sub>-C<sub>22</sub> hydroxyalkane sulfonate or alkyl glyceryl ether sulfonate (AGS); or aromatic sulfonates such as alkyl benzene sulfonate.

30



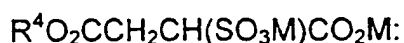
The anionic may also be an alkyl sulfate (e.g. C<sub>12</sub>-C<sub>18</sub> alkyl sulfate) or alkyl ether sulfate (including alkyl glyceryl ether sulfates). Among the alkyl ether sulfates are those having the formula:



wherein R is an alkyl or alkenyl having 8 to 18 carbons, preferably 12 to 18 carbons, n has an average value of greater than 1.0 preferably greater than 3; and M is a solubilizing cation such as sodium, potassium, ammonium or substituted ammonium. Ammonium and sodium lauryl ether sulfates are preferred.

The anionic may also be alkyl sulfosuccinates (including mono- and dialkyl, e.g., C<sub>6</sub>-C<sub>22</sub> sulfosuccinates); alkyl and acyl taurates, alkyl and acyl sarcosinates, sulfoacetates, C<sub>8</sub>-C<sub>22</sub> alkyl phosphates and phosphates, alkyl phosphate esters and alkoxyl alkyl phosphate esters, acyl lactates, C<sub>8</sub>-C<sub>22</sub> monoalkyl succinates and maleates, sulphoacetates, alkyl glucosides and acyl isethionates.

20 Sulfosuccinates may be monoalkyl sulfosuccinates having the formula:

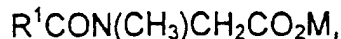


and amide-MEA sulfosuccinates of the formula:



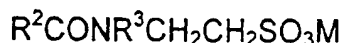
wherein R<sup>4</sup> ranges from C<sub>8</sub>-C<sub>22</sub> alkyl and M is a solubilizing cation.

30 Sarcosinates are generally indicated by the formula:



wherein R<sup>1</sup> ranges from C<sub>8</sub>-C<sub>20</sub> alkyl and M is a solubilizing cation.

Taurates are generally identified by formula:

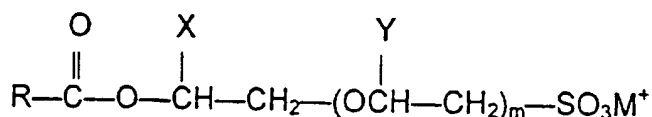


wherein R<sup>2</sup> ranges from C<sub>8</sub>-C<sub>20</sub> alkyl, R<sup>3</sup> ranges from C<sub>1</sub>-C<sub>4</sub> alkyl and M is a solubilizing cation.

Particularly preferred are the C<sub>8</sub>-C<sub>18</sub> acyl isethionates. These esters are prepared by reaction between alkali metal isethionate with mixed aliphatic fatty acids having from 6 to 18 carbon atoms and an iodine value of less than 20. At least 75% of the mixed fatty acids have from 12 to 18 carbon atoms and up to 25% have from 6 to 10 carbon atoms.

Acyl isethionates, when present, will generally range from about 10% to about 70% by weight of the total bar composition. Preferably, this component is present from about 30% to about 60%.

The acyl isethionate may be an alkoxyated isethionate such as is described in Ilardi et al., U.S. Patent No. 5,393,466, hereby incorporated by reference. This compound has the general formula:



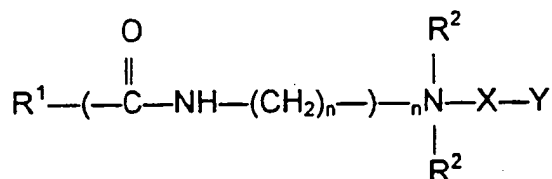
wherein R is an alkyl group having 8 to 18 carbons, m is an integer from 1 to 4, X and Y are hydrogen or an alkyl group having 1 to 4 carbons and M<sup>+</sup> is a monovalent cation such as for example, sodium, potassium or ammonium.

Anionic will generally comprise 1-20% by wt., preferably 5 to 15% by wt. of a composition and one or more anionic may be used.

In particular, preferred anionic is alkali metal (e.g. sodium) lauryl ether sulfate (SLES).

### Amphoteric

Amphoteric detergents which may be used in this invention include at least one acid group. This may be a carboxylic or a sulphonic acid group. They include quaternary nitrogen and therefore are quaternary amido acids. They should generally include an alkyl or alkenyl group of 7 to 18 carbon atoms. They will usually comply with an overall structural formula:



where  $\text{R}^1$  is alkyl or alkenyl of 7 to 18 carbon atoms;

$\text{R}^2$  and  $\text{R}^3$  are each independently alkyl, hydroxyalkyl or carboxyalkyl of 1 to 3 carbon atoms:

$m$  is 2 to 4;

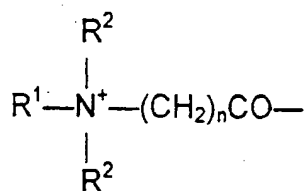
$n$  is 0 to 1;

$\text{X}$  is alkylene of 1 to 3 carbon atoms optionally substituted with hydroxyl,

and

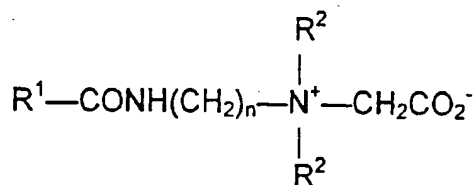
$\text{Y}$  is  $-\text{CO}_2-$  or  $-\text{SO}^3-$

Suitable amphoteric detergents within the above general formula include simple betaines of formula:



5

and amido betaines of formula:



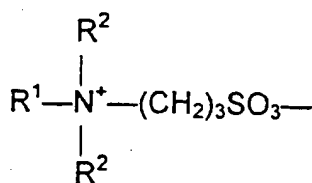
10

15 where n is 2 or 3,

In both formulae  $\text{R}^2$  and  $\text{R}^3$  are as defined previously.  $\text{R}^1$  may in particular be a mixture of  $\text{C}_{12}$  and  $\text{C}_{14}$  alkyl groups derived from coconut so that at least half, preferably at least three quarters of the groups  $\text{R}^1$  have 10 to 14 carbon atoms.  $\text{R}^2$  and  $\text{R}^3$  are preferably methyl.

20

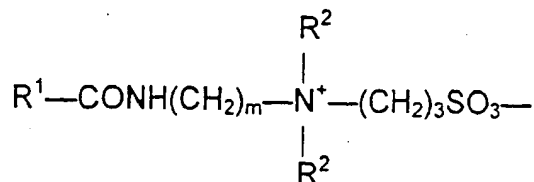
A further possibility is that the amphoteric detergent is a sulphobetaine of formula:



25

30

or



35

where m is 2 or 3, or variants of these in which  $-(CH_2)_3SO_3-$  is replaced  
by



In these formulae  $R^1$ ,  $R^2$  and  $R^3$  are as discussed previously.

Optional nonionic and cationic surfactants may also be used such as are  
10 well known to those skilled in the art.

#### Isoprene Glycol (IPG)

The isoprene glycol should be used in an amount of 0.1 to 7%, preferably  
15 0.5 to 5%, more preferably 1.0 to 5% by wt. of the composition. It should be  
noted that, even when used at an amount as high as 9%, when used alone,  
isoprene glycol does not inhibit freezing. Total ratios of IPG to DAG (discussed  
below) are 1:8 to 7:2, preferably 1:8 to 5:4

#### 20 Dialkylene Glycol (DAG)

Again, the dialkylene glycol (preferably dipropylene glycol) should be used  
in an amount of about 1.5% to about 8.5% by wt., preferably about 3.0% to about  
8% by wt. and ratios are as noted above.

25

#### Optional Ingredients

In addition, the compositions of the invention may include optional  
ingredients as follows:

30

Organic solvents, such as ethanol; auxiliary thickeners, such as  
carboxymethylcellulose, magnesium aluminum silicate, hydroxyethylcellulose,  
methylcellulose, carbopols, glucamides, or Antil<sup>®</sup> from Rhone Poulenc; perfumes;

sequestering agents, such as tetrasodium ethylene diaminetetraacetate (EDTA), EHDP or mixtures in an amount of 0.01 to 1%, preferably 0.01 to 0.05%; and coloring agents, opacifiers and pearlizers such as zinc stearate, magnesium stearate, TiO<sub>2</sub>, EGMS (ethylene glycol monostearate) or Lytron 621 (Styrene/Acrylate copolymers); all of which are useful in enhancing the appearance or cosmetic properties of the product.

The compositions may further comprise antimicrobials such as 2-hydroxy-4,2'4' trichlorodiphenylether (DP300); preservatives such as dimethyldimethylhydantoin (Glydant XL 1000), parabens, sorbic acid etc.

The compositions may also comprise coconut acyl mono- or diethanol amides as suds boosters, and strongly ionizing salts such as sodium chloride and sodium sulfate may also be used to advantage.

Antioxidants such as, for example, butylated hydroxytoluene (BHT) may be used advantageously in amounts of about 0.01% or higher if appropriate.

Cationic conditioners which may be used include Quatrisoft LM-200 Polyquaternium-24, Merquat Plus 3330 - Polyquaternium 39; and Jaguar® type conditioners.

Polyethylene glycol's which may be used include:

Polyox	WSR-205	PEG 14M,
Polyox	WSR-N-60K	PEG 45M, or
Polyox	WSR-N-750	PEG 7M.

PEG with molecular weight ranging from 300 to 10,000 Dalton, such as those marketed under the tradename of CARBOWAX SENTRY by Union Carbide.

Thickeners which may be used include Amerchol Polymer HM 1500® (Nonoxynyl Hydroethyl Cellulose); Glucam DOE 120 (PEG 120 Methyl Glucose Dioleate); Rewoderm® (PEG modified glyceryl cocoate, palmate or tallowate) from Rewo Chemicals; Antil® 141 (from Goldschmidt).

5

Another optional ingredient which may be added are the deflocculating polymers such as are taught in U.S. Patent No. 5,147,576 to Montague, hereby incorporated by reference.

10

Another ingredient which may be included are exfoliants such as polyoxyethylene beads, walnut shells and apricot seeds.

15

The compositions may also contain 0.1 to 15% by wt., preferably 1 to 10% by wt. of a structurant. Such structurants can be used to avoid addition of external structurants (e.g., cross linked polyacrylates and clays) if suspending particles is desired as well as to provide desirable consumer attributes.

20

Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts or ratios of materials or conditions or reaction, physical properties of materials and/or use are to be understood as modified by the word "about".

25

Where used in the specification, the term "comprising" is intended to include the presence of stated features, integers, steps, components, but not to preclude the presence or addition of one or more features, integers, steps, components or groups thereof.

30

The following examples are intended to illustrate the invention further and are not intended to limit the invention in any way.

Unless indicated otherwise, all percentages are intended to be parts by weight.

Example 1 and 2

The following examples were prepared as follows:

5

	Example 1	Example 2
Lauric acid	4.64%	4.64%
Myristic acid	3.87%	3.87%
Palmitic acid	3.87%	3.87%
Potassium hydroxide	3.03%	3.03%
Sodium lauryl ether sulfate (SLES)	7.8%	7.8%
Cocamidopropyl betaine (CAPB)	1.8%	1.8%
Ethylene glycol disteareate (EGDS)	2%	2%
Isoprene glycol (IPG)	2%	4%
Dipropylene glycol (DPG)	7%	5%
Glycerin	2%	2%
Cationic polymer	3.6%	3.5%
Polyoxyethylene alkylether	0.75%	0.75%
Dibutylhydroxytoluene (BHT)	0.05%	0.05%
Tetrasodiumedetate tetrahydrate (EDTA)	0.05%	0.05%
Preservative	0.00075%	0.00075%
Perfume	0.9%	0.9%
Water	To 100%	To 100%



### Processing

- 1) Mixture of potassium hydroxide and water was heated to 70-85°C.  
(mixture-1);
- 5 2) Mixture of fatty acids, BHT, SLES, IPG, DPG and Glycerin was heated to 70-85°C (mixture-2) until becoming quite fluid;
- 3) Mixture-2 was added into mixture-1 with agitation (mixture-3);
- 4) EGDS was added into mixture-3;
- 5) Water, EDTA, CAPB, most cation were mixed, heated to 60°C and then  
10 added into mixture-3;
- 6) Mixture-3 was cooled to 45°C;
- 7) IPG, .01% additional cationic and water were separately mixed with agitation (mixture-4);
- 8) Mixture-4, preservative and perfume were added into mixture-3 and cooled  
15 to 35°C.

### Example 3

In a composition containing IPG and DPG the following data was observed in a soap/SLES/betaine system.

20

	<u>IPG</u>	<u>DPG</u>	<u>-5C stability</u>
	0%	0%	freeze, cannot be pumped out; no good
	0	9	freeze, cannot be pumped out; no good
	1	8	not freeze; good
25	2	7	not freeze; good
	3	6	not freeze; good
	4	5	not freeze; good
	5	4	not freeze; good
	6	3	not freeze; slightly good
30	7	2	not freeze; slightly good
	8	1	freeze, cannot be pumped out; no good
	9	0	freeze, cannot be pumped out; no good

As it clearly shows from the examples, only if IPG and DPG are both used within critical parameters do low temperature stability and pumpability improve.

## Claims

1. A liquid shower gel composition comprising:
  - 5 (a) 1-20% by wt. of a free fatty acid or mixture of free fatty acid;
  - (b) 1-20% by wt. of an alkali metal source;
  - (c) 1-20% by wt. of an anionic surfactant or surfactants;
  - (d) 1-15% amphoteric/zwitterionic surfactant;
  - (e) about 1-7% isoprene glycol; and
  - 10 (f) about 2-8% dipropylene glycol.
2. A liquid shower gel composition comprising:
  - 15 (a) 1-22% by wt. of a fatty acid soap or mixtures of fatty acid soaps;
  - (b) 1-20% by wt. of an anionic surfactant or surfactant;
  - (c) 1-15% amphoteric/zwitterionic surfactant;
  - (d) about 1-7% isoprene glycol; and
  - (e) about 2-8% dipropylene glycol.
- 20 3. A composition according to claim 1, wherein alkali metal source is selected from the group consisting of alkali metal hydroxide; alkali metal carbonate; mono-, di or triethanolamine salts; salts of C<sub>2</sub>-C<sub>4</sub> alkylamines and mixtures thereof.
4. A composition according to claim 3, wherein alkali metal is sodium or  
25 potassium.
5. A composition according to claim 1, wherein composition does not freeze at temperatures above -10°C.
- 30 6. A composition according to claim 5, wherein compositions does not freeze at temperatures above about -5°C.

7. A composition according to claim 1, wherein viscosity is 50 to 8000 cps.
8. A composition according to claim 7, wherein viscosity is 100 to 2000 cps.



Application No: GB 9916322.2  
Claims searched: 1 - 8

Examiner: Michael Conlon  
Date of search: 12 October 1999

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C5D (DHF,DHG,DHX,DHZ,DJB,DJC,DJX,D132)

Int Cl (Ed.6): C11D 3/20

Other: Online: WPI, EPODOC, PAJ

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	US5496489 (Oreal) Example 2	1
A	Derwent Abstract No. 1996-184676 [19] relating to JP080059455 (Kao) 05.03.1996	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

**THIS PAGE BLANK (USPTO)**